PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-294285

(43)Date of publication of application : 20.10.2000

(51)Int.Cl.

H01M 10/40
C08J 5/12
C08J 5/18
C08L101/00
H01M 4/04

(21)Application number : 11-101482

(22)Date of filing : 08.04.1999

(71)Applicant : ASAHI CHEM IND CO LTD

(72)Inventor : KOGA TAKEHIRO
YOKOYAMA CHOMEI

(54) MANUFACTURE OF JOINING BODY FOR POLYMER BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To improve productivity by manufacturing a joining body by processing a temporary joining body at a temperature not less than a melting point of an electrolyte after forming the temporary joining body by processing a laminate composed of an electrode and a high polymer solid electrolyte at a temperature lower than the melting point of this electrolyte.

SOLUTION: A temporary joining body obtained by processing a laminate at a temperature lower than a melting point of a high polymer solid electrolyte, an electrode and this electrolyte easily separate between a positive electrode active material surface and the electrolyte when tearing off these by the contact plane to be put in a state such that a part of the electrolyte does not stick to at least the positive electrode active material surface and a negative electrode active material surface. A required process is only to apply pressure when manufacturing the temporary joining body, and the pressure is set to 0.1 to 50 kgf/cm as line pressure applied to the laminate. A joining body obtained by further processing this temporary joining body at a temperature not less than a melting point of the electrolyte can improve a charge/discharge characteristic of a battery. Even in that case, a required process is only to apply pressure, and the pressure is set to 0.1 to 50 kgf/cm as line pressure applied to the temporary joining body.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS

[Translation done.]

CLAIMS

[Claim(s)]
[Claim 1] The manufacture method of the sheet-like zygote for polymer batteries characterized by being succeedingly processed and manufactured at the temperature beyond the melting point of a solid polymer electrolyte after this sheet-like zygote processes the layered product which consists of an electrode and a solid polymer electrolyte at temperature lower than the melting point of a solid polymer electrolyte and considers as a temporary zygote in the method of manufacturing the long picture sheet-like zygote which consists of the electrode and solid polymer electrolyte for polymer batteries.
[Claim 2] The manufacture method of the sheet-like zygote for polymer batteries characterized by considering as a sheet-like zygote by carrying out roll-press processing at the temperature beyond the melting point of a solid polymer electrolyte succeedingly after carrying out roll-press processing of this layered product at temperature lower than the melting point of a solid polymer electrolyte and considering as a temporary zygote in the manufacture method of a sheet-like zygote according to claim 1, applying tension in the direction of a long picture.
[Claim 3] The manufacture method of the sheet-like zygote for polymer batteries according to claim 2 which the width of face of the electrode of this layered product is below the width of face of a solid polymer electrolyte, and is characterized by carrying out the laminating of the heat-resistant sheet more than the width of face of the solid polymer electrolyte which has the melting point beyond the melting point of a solid polymer electrolyte in both sides of a temporary zygote in the manufacture method of a sheet-like zygote according to claim 2 in case roll-press processing is carried out at the temperature beyond the melting point of a solid polymer electrolyte at least.

[Translation done.]

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the manufacture method of a non-drainage system cell of having used the solid polymer electrolyte.
[0002]
[Description of the Prior Art] A rechargeable lithium-ion battery has a high energy density, it is put in practical use from it being suitable for the miniaturization of the pocket device consisting mainly of a cellular phone and a personal computer, and lightweight-izing, and, also after that, various improvement, such as high-capacity[the further thin-shape-izing, lightweight-izing, and]-izing, is continued. However, the present rechargeable lithium-ion battery is the form (for example, JP,59-37292,B) which filled up the hole section of porosity polyolefine separator with the electrolytic solution, and since the ionic permeability of a polyolefine is very low, where the hole section is filled up with the electrolytic solution, ionic conductivity becomes low as compared with the electrolytic solution. Moreover, it flows into the effect of holding the electrolytic solution with which it was filled up, easily deficiently at a hole outside, since it is also required to secure the adhesion of an electrode and separator further, it is necessary to pack the cell structure by the profound metal vessel, and it is not desirable for thin-shape-izing of a cell, and lightweight-izing.
[0003] On the other hand, since a solid electrolyte does not contain free liquid inside substantially, it is excellent in liquid maintenance nature, danger, such as a liquid spill, is low, since the adhesion of an electrode and an electrolyte is secured by making a zygote with an electrode form, simplification of a package is possible, the further thin-shape-izing, lightweight-ization, etc. are expected, and development is furthered towards the formation of high-energy density of a rechargeable battery.
[0004] It divides roughly into a solid electrolyte and ion-conductive ceramics material and the solid polymer electrolyte are proposed. Among these, the former ion-conductive ceramics material has a frangible characteristic, and zygote formation with an electrode is difficult for it. on the other hand, when the solid polymer electrolyte is excellent in processability and flexibility and it uses for electrochemistry elements, such as a cell, zygote structure formation with an electrode is easy, and change of the interface configuration of the solid polymer electrolyte which followed in footsteps of the volume change of the electrode by ion occlusion discharge is possible -- etc. -- it has a desirable property
[0005] As an attempt of such a solid polymer electrolyte, the alkali-metal salt complex of a polyethylene oxide is British by Wright. Polymer It is reported to Journal, seven volumes, and 319 pages (1975), and the solid-polymer-electrolyte material using polyalkylene ether system material, such as a polyethylene glycol and a polypropylene oxide, a polyacrylonitrile, polyphosphazene, the polyvinylidene fluoride, the polysiloxane, etc. is studied actively since then.
[0006] Usually, in the macromolecule solid-state, these solid polymer electrolytes take the form in which the electrolyte dissolved, and are known as a dry system solid polymer electrolyte. Although they do not have the problem of a liquid spill since these dry system solid polymer electrolytes do not contain the electrolytic solution at all, and excelled very much in safety, charge and discharge current density is limited low, and the cell which it is a problem that ionic conductivity is small compared with the ionic conductivity of the electrolytic solution, and it actually constituted using these has a fault, like cell resistance is high. For this reason, the solid-polymer-electrolyte material which has high ionic conductivity is demanded.
[0007] On the other hand, in order to increase an electrolyte degree of dissociation, or to promote the molecular motion of a macromolecule and to raise ionic conductivity, the so-called gel system solid polymer electrolyte which made the polymer matrix contain the electrolytic solution is known (for example, JP,57-143356,A). Although it has been attained that such a gel system solid polymer electrolyte shows ionic conductivity higher than a dry system solid polymer electrolyte, on the other hand, a mechanical strength falls with the increase in an electrolytic-solution content for obtaining high ionic conductivity, and it has problems, like control of thickness also becomes difficult.
[0008] In addition, although the solid polymer electrolyte which sank the electrolytic solution into the porous body of

electrolytic-solution bloating tendency polymer and which has high intensity and high ionic conductivity is also examined (for example, WO 97/No. 48106), the mechanical strength in the temperature which is a room temperature grade cannot be called still sufficient mechanical strength although improved. This problem has the following technical problems, when manufacturing the long picture zygote which consists of an electrode and a solid polymer electrolyte, in order to raise productivity.
[0009] In order to manufacture a long picture above zygote, the method of piling up an electrode and a solid polymer electrolyte using a roll-press machine, and joining continuously is advantageous to raising productivity. However, in order for the position where an electrode and solid polymer electrolytes overlap in this method to always consider as a fixed thing during manufacture, it is desirable to begin to roll the solid polymer electrolyte rolled in the shape of a roll as well as the electrode rolled in the shape of a roll to the roll-press section, where fixed tension is applied to each. Therefore, with tension, when the weak solid polymer electrolyte of a mechanical strength is used, before being joined in the roll-press section, even if it will be fractured or is joined, deformation and the problem to which the zygote of thickness uniform for deformation is not obtained, but productivity falls will be produced.
[0010] ** which raises the mechanical strength of a solid polymer electrolyte -- ****** -- for example, a monomer and the electrolytic solution are sunk into the textile fabrics used as core materials, such as a polyolefine, etc., and although there are some which reinforced the solid polymer electrolyte with methods, such as carrying out the polymerization of the monomer by heat-treatment, there is a problem that ionic conductivity falls, like the case where polyolefine separator is used
[0011]
[Problem(s) to be Solved by the Invention] Namely, it aims at this invention raising the productivity of a long picture sheet-like zygote which consists of an electrode and a solid polymer electrolyte, and offering the manufacture method which is enough.
[0012]
[Means for Solving the Problem] the sheet-like zygote which is processing at temperature lower than the melting point of a solid polymer electrolyte, making into a temporary zygote the layered product which consists of an electrode and a solid polymer electrolyte first, and processing it at the temperature beyond the melting point of a solid polymer electrolyte succeedingly as a result of inquiring wholeheartedly, in order that this invention persons' may attain the above-mentioned purpose, and consists of an electrode and a solid polymer electrolyte -- productivity -- it was able to attain holding the performance to which the polymer battery using the possible fake bundle and this zygote is equal to manufacturing highly at use
[0013] Namely, this invention (1) The manufacture method of the sheet-like zygote for polymer batteries characterized by being succeedingly processed and manufactured at the temperature beyond the melting point of a solid polymer electrolyte after this sheet-like zygote processes the layered product which consists of an electrode and a solid polymer electrolyte at temperature lower than the melting point of a solid polymer electrolyte and considers as a temporary zygote in the method of manufacturing the long picture sheet-like zygote which consists of the electrode and solid polymer electrolyte for polymer batteries.
(2) The manufacture method of the sheet-like zygote for polymer batteries characterized by considering as a sheet-like zygote by carrying out pressure treatment at the temperature beyond the melting point of a solid polymer electrolyte succeedingly after carrying out pressure treatment of this layered product at temperature lower than the melting point of a solid polymer electrolyte and considering as a temporary zygote in the manufacture method of a sheet-like zygote given in (1), applying tension in the direction of a long picture.
(3) In the manufacture method of a sheet-like zygote given in (2), the width of face of the electrode of this layered product is below the width of face of a solid polymer electrolyte, and in case pressure treatment is carried out at the temperature beyond the melting point of a solid polymer electrolyte at least, it is related with the manufacture method of the sheet-like zygote for polymer batteries given in (2) characterized by carrying out the laminating of the heat-resistant sheet more than the width of face of the solid polymer electrolyte which has the melting point beyond the melting point of a solid polymer electrolyte in both sides of a temporary zygote
[0014] Hereafter, this invention is explained in detail. Although there are two kinds of solid polymer electrolytes, the dry system solid polymer electrolyte which does not contain an electrolytic-solution solvent, and the gel system solid polymer electrolyte swollen in the electrolytic solution, a gel system solid polymer electrolyte has high ionic conductivity, and is more desirable. The solid polymer electrolyte described below in this invention expresses the thing of said gel system electrolyte.
[0015] A solid polymer electrolyte consists of a polymer matrix and the electrolytic solution. Although especially this polymer matrix is not limited, a fluoride vinylidene system copolymer, an acrylonitrile copolymer, a polyacrylate copolymer, a polyethylene-oxide copolymer, etc. can be used, for example. Since it excels chemical-resistant and excels also in electrochemical stability among these in using especially as a polymer battery, a fluoride vinylidene

system polymer is desirable.
[0016] A fluoride vinylidene system polymer makes vinylidene fluoride a principal component, and points out the so-called homopolymer which does not contain the polymer and copolymer containing copolymers, such as hexafluoropropylene, a perfluoro propylene, perfluoro vinyl ether, a tetrafluoroethylene, a hexafluoro propylene oxide, and fluoro ethylene.
[0017] The electrolytic solution dissolves an electrolyte in the organic solvent. Although lithium salt is desirable as an electrolyte and LiAsF6, LiBF4, LiPF6, LiClO4, LiCF3SO3, LiN (CF3SO2)2, LiC (CF3SO2)3, etc. are specifically mentioned, it is not restricted to this. Although those mixed solvents, such as propylene carbonate, ethylene carbonate, gamma-butyrolactone, 1, 2-dimethoxyethane, 1, 3-dioxolane, a tetrahydrofuran, methyl formate, an acetonitrile, dimethyl sulfoxide, 2-methyl tetrahydrofuran, the 3-methyl -1, 3-OKISOZA iridine-2-ON, dimethyl carbonate, methylethyl carbonate, diethyl carbonate, diethylether, and a sulfolane, etc. are mentioned as an example of the organic solvent which constitutes the electrolytic solution for polymer batteries, it is not restricted to this.
[0018] It is desirable that the ionic conductivity of the electrolytic solution is 0.1 or more mS/cm although limitation is impossible since the concentration of the electrolyte which dissolves in the organic solvent changes with combination of an electrolyte and the organic solvent, and when for that LiBF4 is used as an electrolyte and it uses propylene carbonate as an organic solvent, it is desirable that it is [0.1 or more mol/l] 2 or less mol/l. By the concentration not more than this, there are too few electrolytes, or in the concentration beyond this, since the viscosity of the electrolytic solution rises too much, ionic conductivity is not made highly.
[0019] Next, the production method of a solid polymer electrolyte is indicated. A solid polymer electrolyte is produced by making the electrolytic solution hold in a polymer matrix. How to dissolve for example, a polymer matrix in the electrolytic solution, consider as a uniform solution as this concrete method, carry out the cast of this solution, and produce. The method of sinking into a polymer matrix Plastic solid and making it swell the electrolytic solution etc. is mentioned.
[0020] It is the method of cooling and producing, after dissolving by heating a polymer matrix to an elevated temperature in the electrolytic solution as the former more concrete method and carrying out the cast of the solution. After dissolving a polymer matrix in the mixed solvent of plasticizers, such as an acetone and a tetrahydrofuran, and the electrolytic solution, the method of producing by removing by evaporating a plasticizer component etc. is mentioned.
[0021] As a method of sinking in and making the electrolytic solution swelling, the following examples are given to the polymer matrix in the case of the latter. That is, after mixing beforehand the method of applying the electrolytic solution with a spray or the brush, and the 3 above-mentioned electrolyte with a polymer matrix to the method immersed during the bath of the electrolytic solution in 1 polymer matrix, and 2 polymer matrix, liquefied or the method of introducing by the shape of gas is mentioned in the organic solvent. Moreover, you may heat in order to raise a wet out rate in each method.
[0022] Any, such as bulk, a porous body, and a foam, are sufficient as the configuration of the polymer matrix of this invention. Moreover, you may construct a bridge by methods, such as electron beam irradiation, for the purpose of the improvement in on the strength, the improvement in dimensional stability, etc. It is more more desirable not to use a core material etc. from the purpose which makes ionic conductivity high although it is also possible to reinforce by furthermore using a core material etc. When using a heart agent, there is resistance over the electrolytic solution, what has high stability is electrochemically desirable, and the fiber of polyolefine systems, such as polypropylene and polyethylene, etc. is illustrated.
[0023] Although it cannot limit since the amount of the electrolytic solution which a polymer matrix is made to contain changes with a polymer matrix and combination of the electrolytic solution, in the case where it considers as the solution which dissolved in propylene carbonate so that might become a fluoride vinylidene system polymer about a polymer matrix and it might become 1 mol/l about LiBF4 in the electrolytic solution, for example, it is made a weight, and is the 0.1 or more electrolytic solutions to the macromolecule base material 1, and is ten or less. Since ionic conductivity is low stopped by 0.1 or less weight and the intensity of a solid polymer electrolyte falls or more by ten preferably, it is not desirable.
[0024] Furthermore, a polymer battery can be manufactured by combining the solid polymer electrolyte obtained by doing in this way with the positive-electrode electrode used suitable for a cell, and a negative-electrode electrode. Here, although LiCoO2, LiNiO2, and LiMn2O4 grade can be used for a positive-electrode electrode as the active material, an active material is not restricted to these. And at least, with a binder, an active material is supported by one side or both sides as a layer uniform on a metallic foil charge collector, and serves as a positive-electrode electrode.
[0025] Moreover, as a negative-electrode electrode, what consists of carbon, such as a needle coke and graphite, can be supported and created as a uniform layer on a metallic foil charge collector with a binder at least at one side or both sides. In addition, a lithium metal remains as it is and can be considered as a negative-electrode electrode. Next, the

manufacture method of a sheet-like zygote which consists of the electrode and solid polymer electrolyte for polymer batteries in this invention is explained in detail.
[0026] Here, the electrode in this invention and the layered product of a solid polymer electrolyte are the objects piled up so that both the fields where carbon was supported might counter in the field and negative-electrode electrode with which the active material was supported in the positive-electrode electrode of the two electrodes of a positive electrode and a negative electrode through the sheet of a solid polymer electrolyte except a lithium metal. When it has the mechanism in which it is begun to roll an electrode and a solid polymer electrolyte, and the mechanism to heat and specifically produces a temporary zygote at least, if it should just have the mechanism in which the aforementioned layered product is made to form through a solid polymer electrolyte and has the mechanism to pressurize before carrying out temporary junction of the equipment which manufactures a long picture sheet-like zygote in this invention, it is still more desirable.
[0027] It is possible it to be desirable to have the structure which inserts and forms an electrode and a solid polymer electrolyte between the rolls of two shafts, in order to form the aforementioned layered product, to be able to carry out heating pressure treatment easily, while forming a layered product, if a press mechanism and a heating mechanism are offered on the roll of two shafts with such structure, and to consider as a temporary zygote. If it is set as the temperature beyond the melting point of a solid polymer electrolyte further succeedingly, the zygote easily told to this invention can be manufactured.
[0028] Although the heating mechanism in this invention also has a method of what is necessary being just to be able to heat the portion to join, dividing the portion to join in space, and heating only the inside of it, the method of performing, while heating the very thing for the roll of two shafts as described above, and heating a layered product directly is efficient. Moreover, it is also possible to combine the describing [above] 2 methods with maintaining the stable heating state.
[0029] Although it can be decided by differential scan type calorimetric analysis (Following DSC is called) etc. that it will be the melting point of the solid polymer electrolyte in this invention, let temperature of the standup portion of the peak which originates in dissolution of a polymer matrix in DSC in this invention be the melting point. For example, in the solid polymer electrolyte infiltrated so that it might be made a weight, using respectively the solution which dissolved so that might become a poly hexafluoropropylene fluoride vinylidene copolymer (3 % of the weight of hexafluoropropylene contents) as a polymer matrix and it might become propylene carbonate in mol [1 //l.] about $LiBF_4$ as the electrolytic solution and might become the electrolytic solution 3 to the polymer matrix 1, it is about 80 degrees C.
[0030] In this invention, it is characterized by processing the above-mentioned layered product at temperature lower than the melting point of a solid polymer electrolyte, and considering as a temporary zygote first. A temporary zygote exfoliates easily between a positive-active-material side, a solid polymer electrolyte, and a negative-electrode active material side and a solid polymer electrolyte, when an electrode and a solid polymer electrolyte tear off by the plane of composition, and it points out the state where a part of solid electrolyte does not adhere to a positive-active-material side and a negative-electrode active material side at least here.
[0031] Although it will not matter if the temperature which manufactures a temporary zygote is lower than the melting point of a solid polymer electrolyte, it is desirable that it is more than the temperature that the electrolytic solution solidifies in that the ease of treating of a solid polymer electrolyte is excellent. At the temperature not more than this, the electrolytic solution in a solid polymer electrolyte congeals, and since it becomes hard, it becomes lacking in processability. Moreover, at the temperature beyond the solid-polymer-electrolyte melting point, by tension, a solid polymer electrolyte is not desirable in order to fracture, deformation and.
[0032] Although it does not become settled uniquely since the range of desirable tension changes with materials of a solid polymer electrolyte, an upper limit is a load corresponding to the elastic limit in the load-deformation curve of a solid polymer electrolyte, for example, in the case of the polyelectrolyte which sank in the electrolytic solution which dissolved $LiBH_4$ in the polyvinylidene difluoride membrane filter (DEYURAPOA GHVP) by Millipore Corp. so that it ~~might become~~ propylene carbonate in mol [1 / // l. and] under the room temperature, is 70 kgf/cm2 here. Moreover, although not limited especially concerning a minimum, what is necessary is just 1 kgf/cm2.
[0033] Moreover, on the occasion of manufacture of a temporary zygote, you may give the pressure of the range by which a solid polymer electrolyte is not destroyed. Temporary junction of an electrode and a solid polymer electrolyte becomes better by putting a pressure. A concrete pressure is 50 or less kgf/cm more than per kgf/cm more preferably that what is necessary is just 0.1 or more kgf/cm 100 or less kgf/cm as a linear pressure which joins a layered product.
[0034] Although the temporary zygote manufactured by the above method could attain the improvement in productivity, when it performs charge and discharge as a cell, the outstanding charge-and-discharge property is not acquired. For this reason, in this invention, it is characterized by processing further at the temperature beyond the melting point of a solid polymer electrolyte, and considering as a zygote. The processing temperature of zygote

manufacture needs to be beyond the melting point of a solid polymer electrolyte, in order to perform sufficient junction to an electrode and a solid polymer electrolyte. Junction sufficient at processing temperature lower than the melting point is not obtained. Moreover, the upper limit of processing temperature is restricted by the boiling point of the electrolytic solution, the decomposition temperature, etc., and it is necessary to set it up lower than the temperature to which the organic solvent which constitutes the electrolytic solution by processing disperses remarkably, or a pyrolysis happens.

[0035] Since the solid polymer electrolyte is carrying out temporary junction of deformation by tension and fracture not posing a problem like a temporary zygote manufacturing process even if it heats beyond the melting point of a solid polymer electrolyte in zygote manufacture with tension by temporary junction at deformation and the electrode with low possibility of fracturing, the problem by tension is for being dependent on the intensity of an electrode. It can be called that effective that the manufacturing process of ******** exists after the manufacturing process of a temporary zygote [in / this invention / from this point].

[0036] Moreover, it is better to apply a pressure in the manufacturing process of a zygote. It is because junction of an electrode and a solid polymer electrolyte becomes better by putting a pressure. A concrete pressure is 50 or less kgf/cm more than per kgf/cm more preferably that what is necessary is just 0.1 or more kgf/cm 100 or less kgf/cm as a linear pressure which joins a temporary zygote.

[0037] Although the combined use with a roll press and a monotonous press is also possible also for using not a roll press but a monotonous press for pressure treatment, as compared with the case where performing a monotonous press continuously uses an impossible hatchet roll press, productivity is inferior. Moreover, in this invention, when the width of face of a solid polymer electrolyte is wider than the width of face of an electrode, carrying out the laminating of the heat-resistant sheet which has the thermal resistance beyond the melting point of a solid polymer electrolyte above the width of face of a solid polymer electrolyte has an effect in the maximum outside of a layered product. Especially, there is an effect at the time of zygote production.

[0038] At the process of zygote production to which makes it larger generally than the width of face of an electrode in order that a solid-state polyelectrolyte may prevent an inter-electrode short circuit, and manufactures a zygote in many cases, therefore the temperature beyond the melting point of a solid-state polyelectrolyte is applied, a solid polymer electrolyte fuses, it turns to the external surface of a zygote, or adheres to the press side of a roll-press machine, and continuous manufacture is difficult and a problem arises for productivity. Therefore, it is more desirable to use a heat-resistant sheet. The heat-resistant sheet which has the thermal resistance beyond the melting point of a solid polymer electrolyte may cover the whole solid polymer electrolyte, and may cover only the portion which the solid electrolyte protruded from the electrode side.

[0039] if the heat-resistant sheet which has the thermal resistance beyond the melting point of a solid polymer electrolyte has electrolytic-solution-proof nature -- more -- desirable -- concrete -- a polyethylene terephthalate (Following PET is called), a polyimide, an aramid, and a polytetrafluoroethylene (metal sheets, such as polymer sheets called Following PTFE, such as a tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer (Following PFA is called) and an ethylene-tetrafluoroethylene copolymer (Following ETFE is called), and copper, aluminum, -- or paper etc. is mentioned) Among these, it is also possible to use it in the state where it stuck on the portion which the polymer sheet had insulation and the solid electrolyte protruded from the electrode side.

[0040]

[Embodiments of the Invention] Hereafter, an example explains this invention in detail. In the example, the 2 shaft laminator (MAII[by the completion laminator company]-550 type) was used as a heating roll-press machine.

[0041]

[Example 1] Positive-electrode electrode: $LiCoO_2$ powder of 5 micrometers of mean particle diameters was distributed in N-methyl pyrrolidone solution of poly vinylidene fluoride (KFmade from Kureha chemistry- 1100), and the uniform distribution slurry was created. They were the $LiCoO_2$100 weight section and the poly vinylidene fluoride 3 weight section as a solid-content component of this slurry. Subsequently, the afterbaking press which used the doctor blade for the metal aluminium sheet (15 micrometers of thickness), carried out coating of this slurry to one side, and was dried was performed, and the positive-electrode electrode was created. This paint film thickness was 110 micrometers, and the amount of eyes was 265 g/m2.

[0042] Negative-electrode electrode: It mixed in the solution which dissolved spherical graphite (a mesophase carbon micro bead, 10 micrometers of mean particle diameters) in N-methyl pyrrolidone solution of poly vinylidene fluoride (the product made from the Kureha chemistry, KF-1100) to 10wt(s)%, distributed processing was performed, and the slurry distributed uniformly was prepared. In addition, the solid content in a slurry was taken as the graphite 100 weight section poly vinylidene fluoride 8 weight section. this slurry -- a metal copper sheet (12 micrometers of thickness) -- a doctor blade -- using -- one side -- coating -- it dried, and hot press was carried out and the negative-electrode electrode of 77 micrometers of thickness was created The amount of eyes of this paint film was 85g.

[0043] Solid polymer electrolyte: The poly (hexafluoropropylene-fluoride vinylidene) copolymer resin (3 % of the weight of hexafluoropropylene contents) powder was fabricated on the sheet of 35 micrometers of thickness by heating extrusion fabrication using the extruding press machine with an extruding-die temperature of 230 degrees C. After performing electron beam irradiation on the obtained sheet by 10Mrad(s), the hydrogen fluoride (HF) gas which carried out the vacuum drying and which was generated at 80 degrees C was removed. Subsequently, after infiltrating chlorofluocarbon HFC134a as a foaming agent within an airtight container (7 % of the weight of liquid contents), it heated for 10 seconds at 180 degrees C, and the white foam of 70 micrometers of thickness was obtained. The volume fraction to the whole foam of the closed cell measured with the 930 type air relation aerometer was 73 capacity %.
[0044] After having cut this sheet to 100cmx5cm, having put in into the glassware which put in the electrolytic solution which dissolved LiBF4 so that it might become 1.0 mol/l to the mixed solvent of the ethylene carbonate prepared so that it might be set to 1:1 by the volume ratio, and gamma-butyrolactone, decompressing and removing the air in a system, by holding in the dry state and holding under 70-degree-C conditions in the state of sealing to atmospheric pressure for 3 hours at ******, the electrolytic solution was sunk in and the solid polymer electrolyte was created. When the heat balance of this solid polymer electrolyte was measured by the differential scan type heating-value system, the exoergic peak accompanying dissolution was seen from 90 degrees C, and peak temperature was 120 degrees C.
[0045] It inserted so that the coating side of two electrodes might counter through a solid polymer electrolyte by the positive-electrode electrode which cut into 100cmx5cm the solid polymer electrolyte created as mentioned above and by which one side coating was carried out, and the negative-electrode electrode, and the temporary zygote was created by what it lets pass to the roll-press machine warmed at 50 degrees C by syringe ** 6kgf (30 cm/min). It cooled radiationally, after letting this temporary zygote pass to the roll-press machine further warmed at 130 degrees C by syringe ** 6kgf (30 cm/min), and the zygote was obtained. When the part was taken and this zygote was torn off in the perpendicular direction to the field, exfoliation did not take place by the plane of composition of a solid polymer electrolyte and an electrode, but the exfoliation inside the paint film of an electrode was seen. Of course, to the force of the shearing to a direction level to a field, it is resistant, and position gap was not caused.
[0046] 20cmx5cm size is cut from this zygote, and it is sheet metal (the thickness of 50 micrometers) of aluminum in a positive-electrode electrode side as a tab. Copper sheet metal (thickness of 45 micrometers, 1cmx3cm) is attached in a 1cmx3cm and negative-electrode electrode side. An innermost layer and a 20-micrometer aluminium sheet for a 40-micrometer polypropylene sheet An interlayer, It is charge and discharge (constant-current (63mA) constant voltage (4.2V) charge) about the cell which packed the 20-micrometer polyimide sheet by the polymer package of structure made into the maximum sheathing, and was obtained. As a result of carrying out 2.7 V-cut constant-current discharge, the amount of first time electric discharge of 280mAh(s) and first time charge-and-discharge efficiency was possible for 87% and repeat charge and discharge per 1g of negative-electrode active materials, and the 10th charge-and-discharge efficiency was 100%.
[0047]
[Example 2] The temporary zygote which consists of an electrode and a solid polymer electrolyte by the same method as an example 1 is created except the size of an electrode and a solid polymer electrolyte being 300cmx5cm. this temporary zygote -- a 500cmx10cm PTFE sheet (the NITTO DENKO CORP. make --) When it let it pass to the roll-press machine (30 cm/min) which put by two 0.1mm thickness and was warmed at 140 degrees C by syringe ** 6kgf, the zygote which consists of an electrode which was excellent in junction nature like the example 1, and a solid polymer electrolyte was able to be obtained. When the charge and discharge of the same cell as an example 1 were created and carried out using this zygote, 86% and the repeat charge and discharge of the amount of first time electric discharge were possible for 280mAh(s) and first time charge-and-discharge efficiency per 1g of negative-electrode active materials, and the 10th charge-and-discharge efficiency was 99%, and was the cell of a performance almost equivalent to an example 1.
[0048]
[Example 3] The temporary zygote which consists of an electrode and a solid polymer electrolyte by the same method as an example 1 is created except the size of an electrode and a solid polymer electrolyte being 300cmx5cm. both sides of a portion which a solid polymer electrolyte is beginning to see rather than an electrode among these temporary zygotes -- an insulating tape (TERAOKA SEISAKUSHO Make --) A Kapton tape and the thickness of 40 micrometers were stuck, and when it let it pass to the heating roll-press machine (30 cm/min) warmed at 130 degrees C by syringe * 6kgf after an appropriate time, the zygote which consists of an electrode which was excellent in junction nature like the example 1, and a solid polymer electrolyte was able to be obtained. Remains of the melt of a solid polymer electrolyte were not seen. When the charge and discharge of the same cell as an example 1 were created and carried out using this zygote, 86% and the repeat charge and discharge of the amount of first time electric discharge were possible for 280mAh(s) and first time charge-and-discharge efficiency per 1g of negative-electrode active materials, and the

10th charge-and-discharge efficiency was 99%, and was the cell of a performance almost equivalent to an example 1.
[0049]
[The example 1 of comparison] The temporary zygote was obtained using the roll-press machine (30 cm/min) which created the electrode and the solid polymer electrolyte by the same method indicated in the example 1, and was warmed at 50 degrees C by syringe ** 6kgf. Although junction exfoliated comparatively easily by tearing off in the perpendicular direction to a field rather than was perfect, this temporary zygote is resistant to the force of the shearing to a direction level to a field with the liquid contained in a solid polymer electrolyte, and did not cause position gap.
[0050] As a result of cutting a 20cmx5cm portion from this temporary zygote and carrying out charge and discharge by the same method as an example 1, 180mAh(s) and first time charge-and-discharge efficiency have [the amount of first time electric discharge] 78% and a low and performance per 1g of negative-electrode active materials, and although repeat charge and discharge are possible, 90% and capacity retention are also low at the 5th charge-and-discharge efficiency. From this, it was shown that a temporary zygote has an inadequate cell performance.
[0051]
[The example 2 of comparison] When it let it pass to the roll-press machine (30 cm/min) which created the electrode and the solid polymer electrolyte by the same method indicated in the example 1, and was warmed at 130 degrees C by syringe ** 6kgf, a solid polymer electrolyte was not able to fuse in roll this side, it was not able to pile up in roll this side, and the zygote which consists of an electrode and a solid polymer electrolyte was not able to be obtained.
[0052]
[The example 3 of comparison] Although the layered product creation which consists of an electrode and a solid polymer electrolyte by the same method as an example 2 was tried except not using a PTFE sheet, when it let it pass to the roll-press machine (30 cm/min) warmed at 140 degrees C by syringe ** 6kgf, a part of solid polymer electrolyte overflowing into the electrode exterior was not able to fuse, and the zygote which remains to roll this side and consists of an electrode and a solid polymer electrolyte at first was not able to be obtained.
[0053]
[Effect of the Invention] According to the manufacture method of the polymer battery of this invention, the problem of the film on-the-strength fall seen at the time of layered product heating can be solved, manufacture of a continuous polymer battery is attained, and a highly efficient polymer battery can be offered efficiently.

[Translation done.]